

UDC 666.762.11:666.3.022.69:666.3.046.4

## USE OF ADDITIVES FORMING LIQUID PHASE IN FIRING IN CORUNDUM CERAMICS TECHNOLOGY (A REVIEW)

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Translated from Steklo i Keramika, No. 10, pp. 31–34, October, 2003.

Additives used in corundum ceramics technology, which form a liquid phase in firing, are classified. The main principles that should be taken into account in selecting additives to ensure production of high-quality aluminum oxide materials with a decreased sintering temperature are formulated. A series of eutectic systems is proposed, whose introduction in corundum makes it possible to obtain dense ceramic materials at a firing temperature of 1350–1550°C. Some sintering specifics of these materials are discussed.

The progress of science and engineering today is unthinkable without ceramic materials with a high level of properties. One of the leading places is taken by ceramics based on  $Al_2O_3$  [1–4]. However, a rather high sintering temperature needed for these materials calls for new technological solutions, since the production of traditional type of ceramics is becoming non-competitive. It is currently impossible to replace such ceramics by other materials with the same (or at least similar) properties and a lower production cost.

One of the main methods for improving competitiveness of corundum ceramics is to lower its sintering temperature, which can be achieved by introducing sintering additives. Evidently, these additives should not only ensure sintering of ceramics at decreased temperatures (1350–1550°C for corundum materials), but should not impair valuable properties of the main phase and, which is most essential, provide for high technological parameters of ceramics. The most promising are additives that form a liquid phase in firing.

Additives of this group used in technology of corundum ceramics and properties of materials are described in [5]. Analysis of those data makes it possible to divide all additives into several subgroups.

The first subgroup includes additives of the type  $R_nO - Al_2O_3 - SiO_2$  and  $R_mO - Al_2O_3 - SiO_2$  ( $R_n$  and  $R_m$  are cations of alkali and alkali-earth metals, respectively). These systems were the first to be investigated in our country in 1950s. Additives of the type  $R_nO - Al_2O_3 - SiO_2$  did not find wide application, since it was impossible to obtain dense ceramics with a high level of properties. Additives  $R_mO - Al_2O_3 - SiO_2$  were researched in detail up to 1980s. The upgrade of production method and use of purer and

more active raw materials made it possible to develop ceramics with porosity less than 2% and a sintering temperature of 1450°C. The bending strength of such ceramics is around 300 MPa. The first samples could reach this level of porosity only after sintering at 1600°C. Among the additives of this subgroup, one can distinguish additives comprising the  $CaO - Al_2O_3 - SiO_2$  system, which was the object of most studies [1, 6]. It should be noted that  $RO$  in this case can be replaced by a number of other oxides, for instance,  $Y_2O_3$ .

Nearly simultaneously with the first subgroup, foreign and then domestic researchers in the USSR started investigating additives of the type  $R_xO_y - TiO_2$  comprising the second subgroup. The research of systems of this type continues up to date. The best samples of ceramics containing the specified additives sinter at 1350–1450°C, reach open porosity less than 1%, and have bending strength at a level of 390 MPa.

The third group includes additives of the type  $R_nO - B_2O_3 - SiO_2$ . The earliest studies of these systems were carried out in 1950s, however, these additives continue attracting attention of researchers. These additives were used to obtain dense ceramics with a sintering temperatures of 1450°C and bending strength equal to 250–270 MPa.

The fourth subgroup contains additives representing a combination of additives from the first three subgroups:  $R_1O - R_2O - B_2O_3 - SiO_2 - TiO_2$  ( $R_1$  and  $R_2$  are alkali-earth cations). Such additive usually contains one or two  $RO$  oxides and two of the three “acid” oxides. The use of additives from the fourth subgroup makes it possible at 1450°C to obtain ceramics with virtually zero porosity and bending strength of 370–420 MPa.

Preference in recent years is given to additives containing more than three components, which are selected not just to ensure a minimal melting temperature in the system, but also taking into account the functional significance of each oxide

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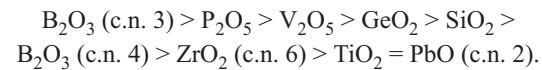
and their effect on microstructure and properties of materials. By selecting an additive composition to provide for the formation of a eutectic melt in the system in firing it is possible to achieve a high degree of compaction at 1350 – 1550°C, while preserving a finely crystalline structure with subsequent crystallization of the melt, which makes it possible to obtain ceramics that virtually does not contain a vitreous phase.

Until now the selection of modifying additives has been usually performed based on accumulated experimental data. Most studies are focused on considering applicability of a particular additive with respect to ensuring the process of rearrangement and capillary attraction of particles, the main attention being paid to the temperature of formation of the liquid phase in the system; other factors are usually not considered [6, 7]. However, for a more comprehensive justified approach to selection of additives it is necessary to study the liquid phase structure, since it has a significant effect on the sintering process in general. Such problem was formulated as early as 1956 [6]. However, this problem up to date has not been considered in the contemporary special literature.

Considering the specifics of the effect of the liquid phase structure on sintering, it should be noted that the most satisfactory among the known liquid structure model is the Stewart cybotactic model [8]. Cybotactic groups (i.e., sites of the melt with a particular type of special packing of particles not having clearly defined boundaries) have a significant role only when the solid phase dissolves in the liquid phase. Sinterability of systems, in which solubility is absent, is mainly controlled by the size of the solid phase particles, the surface tension of liquid and its quantity. For real systems existing in high-melting nonmetallic and silicate materials, the solid phase is found to be dissolved in the liquid phase. The most significant processes occurring in sintering are the reaction on the surface of the solid body and the diffusion process in the volume of the liquid phase [9]. One of the most principal prerequisites ensuring efficiency of these processes from the point of view of thermodynamics is a minimum possible amount of free energy.

It is known from physical chemistry that the phase most easily crystallizing in a melt is the one whose short-range order correlates with the cybotactic groups existent in the melt. Consequently, the optimum conditions for crystallization from the melt (minimum free energy of the system) are implemented in the case when cybotactic groups correlating with the short-range order of the high-melting phase have been prepared within the system. With respect to corundum ceramics, it should be noted that since the coordination number (c.n.) of the aluminum ion in corundum is equal to six, an additive should ensure c.n. 6 for the aluminum ion in the melt. The latter is especially important, since  $\text{Al}_2\text{O}_3$  is an amphoteric oxide. If the liquid phase is acid, the c.n. of the aluminum ion is equal to six, and with a base liquid phase it is equal to four. Thus, the main condition of sintering should be satisfied by introducing additives to ceramics providing for an acid melt.

According to the electron-coordination theory [8], an acid is a material whose particles can accept an electron pair with formation of a coordination bond. The carrier of the electron pair in silicate-oxide melts is the  $\text{O}^{2-}$  ion, consequently, an oxide capable of forming complicated cation-oxygen complexes will have acid properties. A measure of acidity is the ratio of the energy of the element – oxygen bond ( $E_{\text{M}-\text{O}}$ ) to the c.n. of the cation. A correlation of these values indicates that the acid properties of oxides decrease in the following order [2, 8]:



The use of  $\text{P}_2\text{O}_5$  in ceramics technology is not advisable, since its volatility prevents precise control of its chemical composition and can be a reason for fluctuations in the technological parameters of products.

The use of  $\text{B}_2\text{O}_3$  in the technology of structural ceramics is rather limited due to low strength of the vitreous phase formed after firing, although some studies have been focused on additives containing  $\text{B}_2\text{O}_3$  [10].

All types of ceramics based on  $\text{Al}_2\text{O}_3$  contain specially introduced modifying additives improving service properties of ceramics. Obviously, it is desirable for the modifying oxide to be a part of a multicomponent sintering additive that should belong to a system of the type  $\text{M}_m\text{O}_y - \text{Al}_2\text{O}_3 - \text{M}_k\text{O}_y$  ( $\text{M}_m$  is the metal cation of the modifying oxide;  $\text{M}_k$  is an “acid” cation, for instance, cation of vanadium, silicon, or boron).

The selection of a modifier oxide is a sufficiently complex problem. The following requirements should be fulfilled with this respect.

The modifier oxide should, if possible, provide for the crystallization of the additive after cooling. In such case the mechanical properties of the system will be optimum. Additives of eutectic compositions are the most promising in this respect. It should be noted that many additives decreasing the sintering temperature of ceramics and forming a melt in sintering, are present in the end product in the form of glass, which impairs the physicomechanical parameters of the product.

The value of energy of the modifying cation – oxygen bond in a multicomponent melt has a significant effect on the sintering process. The bond energy  $E_{\text{M}-\text{O}}$  is characterized by the ionic potential of the cation  $\phi$ :

$$\phi = \frac{Z}{r},$$

where  $Z$  is the ion charge;  $r$  is the ion radius.

With excessively high bonding energy of oxygen and a high ionic potential, an effect of intense interaction between oxygen ions from the melt and the modifier ions is observed, consequently, the oxygen ions flow away from the aluminum ion, and the c.n. of the latter decreases. This phenomenon increases the energy barrier that the system has to overcome

TABLE 1

Ion $M_m$	Melting point, °C (ion $M_k$ )					
	Si <sup>4+</sup>	Ti <sup>4+</sup>	Zr <sup>4+</sup>	V <sup>5+</sup>	Pb <sup>2+</sup>	Ge <sup>4+</sup>
Li <sup>+</sup>	855	1068	1599	523	854	864
Mg <sup>2+</sup>	1493	1503	1887	596	854	1096
Ca <sup>2+</sup>	1356	1278	1278	598	854	1107
Cu <sup>2+</sup>	1007	1144	1144	627	616	1107
Zn <sup>2+</sup>	1337	1296	1640	581	848	1107
Ba <sup>2+</sup>	1277	1172	1586	492	854	1104
Mn <sup>2+</sup>	1125	1042	1435	627	854	1091
Fe <sup>2+</sup>	1115	1248	1314	627	854	—
Co <sup>2+</sup>	1548	1310	1750	620	854	—
Ni <sup>2+</sup>	1548	1660	1673	627	854	—
Sc <sup>3+</sup>	1548	1660	1710	627	854	1107
Ga <sup>3+</sup>	1516	1700	1720	627	854	1107
Y <sup>3+</sup>	1548	1700	1672	627	854	1107
Bi <sup>3+</sup>	792	788	805	627	700	805
Cr <sup>3+</sup>	1673	1660	1826	627	749	1107
Fe <sup>3+</sup>	1582	1737	1594	620	666	—
Ti <sup>4+</sup>	1490	1705	1524	627	854	1107
Zr <sup>4+</sup>	1548	1524	1890	627	854	1107
Sn <sup>4+</sup>	714	1617	1458	627	834	1107
Pb <sup>4+</sup>	660	854	900	434	865	648
Nb <sup>5+</sup>	1404	1404	1404	627	854	1084
Ta <sup>5+</sup>	1491	1605	1887	627	854	1107
W <sup>6+</sup>	1163	1163	1163	627	669	1107

(the most favorable energy state is when the coordination numbers are equal. Accordingly, this significantly complicates the sintering process.

In the case of too low energy  $E_{M-O}$  and a low potential, oxygen ions are weakly bonded to the modifier cation, the oxygen cations increase the c.n. of aluminum, consequently, its mobility decrease, which also complicates the sintering process.

In addition to the above requirements, another most important prerequisite requires selecting an additive with a minimum possible temperature of liquid phase formation in the multicomponent system. This temperature can be calculated based on the known A. S. Berezhnoi's equation [11].

$$T_{\min} = T_2 \left( \frac{T_2}{T_1} \right)^{1-2/n},$$

where  $T_1$  and  $T_2$  are the minimum melting temperatures of the components and binary eutectics, respectively;  $n$  is the number of components.

The geometrical and electrostatic factors as well should be taken into account in selecting an additive. It is known from the theory of kinetics of heterogeneous processes that a prerequisite for a reaction take place on the interface of two phases is preservation of electric neutrality of the particular surface. Accordingly, when, for instance, two aluminum ions from the solid phase surface pass into the liquid phase, the disturbed electroneutrality should be compensated by liquid phase ions adsorbed on active centers of the solid phase. The charge of these ions should be equal to 6+. Provided that the

"acid" cation has the charge of 4+, the charge of the modifier ion should be equal to 2+. However, this is not the only combination of charges. The requirements of electroneutrality can be satisfied as well in a combination of ions with charges of 1+ and 5+. Thus, according to the surface electroneutrality rule, one of the cations should have a charge lower than that of aluminum and the second one higher than aluminum.

The geometrical rule requires that the initial lattice deformation energy typical of  $Al_2O_3$  and depending on chemical and thermal prehistory should be maintained (at least not grow) on the surface, on which chemical reaction takes place. Aluminum ions in corundum occupy two out of three octahedral vacancies, therefore, when cations pass into the melt, two positive ions should be adsorbed on emerging active centers, not to increase the distortion of the lattice. This condition can be satisfied by ions, one of which is larger than aluminum ion and the second one smaller.

Taking into account the above regularities, an attempt was made to estimate the minimal temperature of emergence of a liquid phase in the systems  $M_mO_y - Al_2O_3 - M_kO_y$ . In the beginning we excluded oxides normally existing in the gaseous state and well as oxides of rare and scattered elements from the list of  $M_mO_y$  oxides. The results of calculating  $\varphi$  indicate that one can exclude as well cations with minimum energy  $E_{M-O}$  ( $\varphi \approx 10 \text{ nm}^{-1}$  and less) and ions with maximum energy  $E_{M-O}$  ( $\varphi \approx 100 \text{ nm}^{-1}$  and more) from the number of ions. For remaining compositions the minimum melting temperatures were calculated (Table 1).

Thus, since the most available "acid" oxide used in ceramic technology is  $SiO_2$ , the optimum properties will be found in additives, where  $M_m$  is  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$ , and  $Cu^{2+}$ .

The use of additives ensuring the formation of a eutectic melt in the course of sintering makes it possible to lower the temperature of sintering of corundum ceramics to 1350–1550°C. The ceramics in this case is characterized by substantial density, a finely crystalline structure (corundum crystal size 3–4  $\mu\text{m}$ ), and sufficiently high strength. After cooling, the eutectic melt crystallizes, and a vitreous phase is completely absent from the material. Additives of such type, as well as properties of ceramics produced with these additives are listed in Table 2.

One of the problems in the technology of high-melting nonmetallic and silicate materials is analyzing the regularities of sintering in ceramics based on  $Al_2O_3$  in the presence of low-melting eutectic additives.

It is known that the sintering process in this case can proceed in one of two directions. The first variant: a solid phase is insoluble in the liquid phase, and sintering proceeds due to surface tension forces. According to the data in [9], in this case the amount of the liquid phase in the system should be at least 25–30%. The second variant: sintering is a three-stage process including rearrangement of solid particles, dissolution-precipitation, and formation of a solid skeleton. These processes are usually not clearly divided in

TABLE 2

Composition of additive (system)	Eutectic formation temperature, °C	Weight content of additive, %	Sintering temperature, °C	Mean density, g/cm <sup>3</sup>	Three-point bending strength, MPa
MnO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub> + 20% ZrO <sub>2</sub>	1145	4.0	1450	4.18	550
FeO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub> + 20% ZrO <sub>2</sub>	1115	4.0	1450	4.16	610
ZnO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub> + 20% ZrO <sub>2</sub>	1337	4.0	1500	4.00	490
MnO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub>	1140	4.0	1450	3.65	370
FeO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub>	1115	4.0	1450	3.56	310
ZnO – Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub>	1337	4.0	1500	3.60	310
MnO – TiO <sub>2</sub>	1290	1.0 – 2.5	1300 – 1500	3.70	280
MnO – TiO <sub>2</sub> + MgO	1290	1.0 – 1.5	1500 – 1550	3.75	310
MgO – TiO <sub>2</sub>	1503	3.0	1550	3.80	320
MgO – SiO <sub>2</sub>	1493	3.0	1550	3.68	280
MgO – ZnO – SiO <sub>2</sub>	1347	3.0	1550	3.72	290
CaO – ZnO – SiO <sub>2</sub>	1170	3.0	1500	3.70	320
CaO – ZnO – SiO <sub>2</sub> + MgO – SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> – SiO <sub>2</sub> *	–	5.0 – 20.0	1450 – 1500	3.50 – 3.75	250 – 350

\* Temperature of eutectic formation: 1170°C for CaO – ZnO – SiO<sub>2</sub> system; 1493 °C for MgO – SiO<sub>2</sub> system; and 1595°C for Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> system.

time, occur simultaneously, and affect each other. Dissolution-precipitation can be controlled either by the kinetics of the chemical reaction on the solid-liquid interface, or by diffusion of reaction products via the boundary layer.

The kinetics of sintering of aluminum oxide ceramics with small quantities of eutectic additives was investigated by the method of non-isothermal sintering [12]. Analysis of the regularities of ceramics sintering based on various types of initial materials with different eutectic additives [13, 14] suggests that sintering occurs in two stages in each case: activation energy of the first stage  $E_1$  varies within wide limits (from 140 to 360 kJ/mole) depending on molding pressure (50 – 400 MPa). Under a constant molding pressure, with a varying amount of sintering additive and various initial materials the value  $E_1$  remains constant. Hence it follows that kinetics at the first stage depends only on molding pressure, i.e., on the geometry of the contact sites of particles in the sample. An increase in molding pressure results in more compact packing of particles, which complicates their migration in microvolumes at the initial stage of sintering and increases apparent activation energy.

The activation energy of the second stage of the process  $E_2$  depends on the dispersion of particles of initial aluminum oxide and does not depend on molding pressure and on the quantity of sintering additive. Thus, the value  $E_2$  directly correlates with the dissolution-precipitation process. The energy barrier that the system has to overcome is presumably determined by the physicochemical prehistory of initial material: changing to a more active and disperse material decreases this barrier and facilitates a more intense process at a lower temperature.

One should note a specific feature typical of all materials considered: transition from one mechanism to the other occurs at the same temperature approaching the temperature of formation of a liquid phase in a multicomponent system, regardless of the kind of materials used.

Thus, sintering of materials considered depends on the size of the high-melting phase particles and the quantity of the sintering additive, more than on other factors. The kinetic process occurs in two stages: prior to the formation of the liquid phase in the system the main mechanism controlling sintering is rearrangement of particles of the high-melting phase. After formation of the liquid phase, dissolution-precipitation becomes the main kinetic process in the system.

Application areas of ceramics developed using the above regularities are quite extensive. Such materials can be used in electronics, as tap gaskets, thread carriers in textile machines, electric insulators, cutting tools, metal-ceramic parts, in medicine, in agriculture machine parts, wear-resistant milling bodies, nozzles for spraying liquids and suspensions, plungers and packing rings for pumps, bearings for precise mechanisms, and other fields of engineering.

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